

COMPETITION AND COEXISTENCE OF MAGNETIC AND QUADRUPOLAR ORDERING

P. FAZEKAS and A. KISS

*Research Institute for Solid State Physics and Optics,
P.O.B. 49, H-1525 Budapest 114, Hungary*

Abstract. The large number of low-lying states of d - and f -shells supports a variety of order parameters. The effective dimensionality of the local Hilbert space depends on the strength, and kind, of intersite interactions. This gives rise to complicated phase diagrams, and an enhanced role of frustration and fluctuation effects. The general principles are illustrated on the example of the effect of a magnetic field on quadrupolar phase transitions in some Pr-based skutterudite compounds.

1. Introduction

Transition metal and rare earth compounds show a rich variety of collective behavior: various kinds of ordered phases as well as strongly fluctuating states (spin and orbital liquids). The basic reason is that d - and f -shells have a relatively large number of low-energy states. Crystal field splitting usually reduces this number (the dimensionality \mathcal{D} of the local Hilbert space) considerably below the free ion value, but complicated physics can arise even from $\mathcal{D} = 3$ or 4.

Let us briefly consider some examples. $\mathcal{D} = 3$ is, in one interpretation, the case of $S = 1$ spin models which turned out to have unanticipated phases like the spin nematics [1]. A different realization is offered by interacting f -electron models based on the low-lying quasi-triplet of Pr ions in $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$ where the nature of Pr ordering is still an open issue [2, 3]. A literal realization of $\mathcal{D} = 4$ is offered by the Γ_8 ground state of Ce ions in CeB_6 which has a rich phase diagram [4]. Alternatively, we may think of the fourfold quasidegeneracy arising from the combination of twofold spin degeneracy with twofold orbital degeneracy, which is the simplest model of d -electrons which is capable of supporting either spin or orbital order, or a combination of both. Twofold orbital degeneracy may occur in cubic, tetragonal, and hexagonal environments, and there are quite different versions of the e_g -model. In the cubic e_g model, orbital

momentum is completely quenched, but orbital order may still break time reversal invariance in the octupolar phase [5]. In contrast, the trigonal e_g states sustain permanent orbital momentum along the threefold axis; such a model should be relevant for understanding the complex behavior of BaVS₃ [6, 7]. The possibilities of $\mathcal{D} > 4$ models are largely unexplored, but we should mention the $\mathcal{D} = 6$ t_{2g} -models of LaTiO₃. There is an intricate relationship between orbital ordering and spin ferromagnetism which would be remarkably difficult to explain without due consideration of the orbital degrees of freedom [8].

As implied above, the definition of \mathcal{D} is not straightforward: it is usually higher than the degeneracy of the ground state level (which would often be small because of small low-symmetry components of the crystal field), but it is not so high as the free-ion value. In CeB₆, the fourfold degenerate Γ_8 level is well separated from the higher-lying Γ_7 which still arises from the Hund's rule ground state; in PrBa₂Cu₃O_{7- δ} , a low-lying doublet and a singlet can be lumped together to give a quasi-triplet which would have Γ_5 character if the symmetry were cubic; but it is, in fact, only tetragonal. In any case, the relevant dimensionality $\mathcal{D} = 3$ is much smaller than 9 which would be the Hund's rule value. It depends primarily on the strength of intersite interaction, which splittings should be considered small.

The highest symmetry of the $\mathcal{D} = 3$ models would be SU(3), etc. Clearly, the exact realization of a high-symmetry model is more than improbable, and if it were really required, we should forget about it. However, there are indications that the domain of influence of such a seemingly artificially high symmetry point in parameter space extends over a substantial portion of the phase diagram [7]. It stands to reason that SU(\mathcal{D}) models (which have symmetries connecting spin and orbital axes in Hilbert space) are more quantum fluctuating than the pure SU(2) spin models: there are more transverse directions to fluctuate to. For instance, the SU(4) model on the triangular lattice has a plaquette resonating ground state (the SU(4) version of the resonating valence bond idea [9]), and the influence of this spin-orbital liquid state may extend to physically relevant regions of the parameter space [10].

Limitation of space forbids us to present more than one concrete example of spin-orbital models. We consider Pr-filled skutterudites, in particular PrFe₄P₁₂ which we model as a $\mathcal{D} = 4$ system.

2. The case of PrFe₄P₁₂

Pr-filled skutterudites show varied behavior: PrRu₄P₁₂ has a metal-insulator transition [13], PrOs₄Sb₁₂ is thought to be an exotic superconductor [14], while PrFe₄P₁₂ remains a normal metal in the entire temperature

range studied so far. Our interest lies in $\text{PrFe}_4\text{P}_{12}$ which in a certain parameter range can be characterized as a heavy fermion system with exceptionally high electronic specific heat [11]. $\text{PrFe}_4\text{P}_{12}$ has a phase transition at $T_{\text{tr}} \approx 6.5\text{K}$ to an ordered phase which had first been thought to be antiferromagnetic, but mounting evidence indicates that it is, in fact, antiferroquadrupolar (AFQ) [11, 15, 12].

Our purpose is to model the AFQ transition by a crystal field model of the $4f$ electrons. We assume that Pr is trivalent ($4f^2$). This can not be literally true, since the driving force of the formation of a heavy band is presumably the admixture of other valence states. However, high-field studies show that the heavy fermion state competes with AFQ ordering [11], so a localized f -shell description should be acceptable within, or adjacent to, the AFQ phase. Besides, at low fields H and high temperatures T , thermal dehybridization acts to obviate the need to consider interband coherence effects.

2.1. THE CRYSTAL FIELD MODEL

The $J = 4$ manifold of Pr^{3+} is split by the approximately cubic crystal field into the Γ_1 singlet, the Γ_3 doublet, and the Γ_4 and Γ_5 triplets¹. Group theory does not tell us the sequence of the states, but fitting the measurements narrows the choice. Analyzing the anisotropy of the magnetization curves, it was concluded that the likely possibilities are: a Γ_1 ground state and a low-lying excited state Γ_4 (the Γ_1 – Γ_4 scheme); or the Γ_1 – Γ_5 scheme; or the Γ_3 – Γ_4 scheme [11]. Similar schemes were suggested for $\text{PrOs}_4\text{Sb}_{12}$ [14, 16].

The assumption that the low- T ordered state is AFQ, seems to speak in favour of the Γ_3 – Γ_4 scheme, since then the ionic ground state Γ_3 possesses a (permanent) quadrupolar moment. It was also pointed out that the choice of the Γ_3 ground state is consistent with a symmetry analysis of the structural distortion accompanying the AFQ ordering [12]. This latter argument relies only on the assumption of the Γ_3 ground state, and does not consider the effects of the low-lying excited state. Here we show that the assumption of the Γ_1 – Γ_4 scheme is also capable to account for most of the observed static properties of $\text{PrFe}_4\text{P}_{12}$.

We now discuss the consequences of assuming a Γ_1 – Γ_4 level scheme. Since the singlet ground state

$$|\Gamma_1\rangle = \sqrt{\frac{5}{24}}(|4\rangle + |-4\rangle) + \sqrt{\frac{7}{12}}|0\rangle \quad (1)$$

¹ The symmetry group is really not O_h , but the tetrahedral T_h . We nevertheless use the cubic classification, which is an approximation at zero field, but when $H \neq 0$, the symmetry will be in any case substantially lowered.

does not carry any kind of moment, the ordered quadrupolar moment has to be induced by intersite interactions, assuming that the local Hilbert space contains also the triplet

$$|\Gamma_4^+\rangle = \frac{1}{4} \left\{ |3\rangle + |-3\rangle + \sqrt{7}(|1\rangle + |-1\rangle) \right\} \quad (2)$$

$$|\Gamma_4^0\rangle = \frac{1}{\sqrt{2}} (|-4\rangle - |4\rangle) \quad (3)$$

$$|\Gamma_4^-\rangle = \frac{1}{4} \left\{ |3\rangle - |-3\rangle + \sqrt{7}(|-1\rangle - |1\rangle) \right\}, \quad (4)$$

where we have chosen the basis of quadrupolar eigenstates. Choosing the energy of (1) as the zero, the states (2)–(4) lie at the level Δ .

The possible moments in the four-dimensional local Hilbert space spanned by (1)–(4) are given by the decomposition

$$(\Gamma_1 \oplus \Gamma_4) \otimes (\Gamma_1 \oplus \Gamma_4) = 2\Gamma_1 + \Gamma_3 + 3\Gamma_4 + \Gamma_5. \quad (5)$$

Evidently, the system could support either dipolar (Γ_4), or either of two kinds of quadrupolar (Γ_3 or Γ_5) order². The quadrupolar order parameters are the same that appear in the decomposition of a purely Γ_4 system

$$\Gamma_4 \otimes \Gamma_4 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5, \quad (6)$$

i.e., they are not sustained by inter-level matrix elements³. – It may be of some interest to mention that the Γ_1 – Γ_4 scheme does not offer the possibility of octupolar order (but the Γ_3 – Γ_4 scheme would).

2.2. THE EFFECT OF EXTERNAL MAGNETIC FIELD

Our decomposition (5) allows to seek dipolar and/or quadrupolar ordering in the system. Experiments give the clue that we should, in fact, look for (antiferro)quadrupolar order. We may rather arbitrarily assume that it is of the Γ_3 kind⁴, i.e., the possible order parameters are $\mathcal{O}_2^0 = 3J_z^2 - J(J+1)$ and $\mathcal{O}_2^2 = J_x^2 - J_y^2$. Furthermore, since the total energy expression for a pair of sites has only tetragonal (as opposed to cubic) symmetry, we need not assume that the \mathcal{O}_2^0 and \mathcal{O}_2^2 couplings would be equal, and we may seek,

² This is a classification of order parameters which can be defined purely locally. $Q \neq 0$ order needs further discussion.

³ In contrast, matrix elements between Γ_1 and Γ_4 would bring extra possibilities of dipolar ordering. This does not seem to be relevant for $\text{PrFe}_4\text{P}_{12}$.

⁴ Assuming \mathcal{O}_{xy} -type Γ_5 ordering would give similar results.

say, \mathcal{O}_2^2 -type order. Using a mean field decoupling, our problem would be rather similar to a four-state Blume–Emery–Griffiths model.

It is a well-known feature of quadrupolar ordering that its phenomenology closely imitates that of antiferromagnetic transitions, though the underlying order parameter is non-magnetic. The phase diagram in the H – T plane (H : magnetic field) was mapped in [11]. The salient features are the following: A sufficiently strong field applied in any direction will suppress AFQ ordering completely. On the phase boundary, a low-field regime of continuous transitions is separated by a tricritical point ($H^* \approx 2$ Tesla, $T^* \approx 4$ K) from the high-field regime of first-order transitions. This change in the character of the phase transition is shown in the field dependence of the specific heat. The nature of the magnetization curve changes drastically at T^* . For $T < T^*$, there is a steplike metamagnetic transition corresponding to the first-order transition from the low- T ordered phase to the disordered phase. For $T^* < T < T_{\text{tr}}(H = 0) \approx 6.5$ K, there is a kind of a smooth metamagnetic transition, where the system crosses the second-order part of the phase boundary. For $T > T_{\text{tr}}(H = 0)$, the magnetization curve is completely smooth. We will show that a mean field treatment of the AFQ transition in the Γ_1 – Γ_4 scheme accounts for these observations quite well.

In the absence of an external magnetic field, Γ_3 and Γ_4 type order parameters (i.e., quadrupolar moment and magnetization) are decoupled because the former is invariant under time reversal, while the latter changes sign. Switching on the magnetic field breaks time reversal invariance, allowing that quadrupolar moment and magnetization get mixed. We can also say that magnetic field, though it couples directly to the angular momentum \vec{J} , may also induce quadrupolar moment.

This is best illustrated by looking at the matrix which contains the matrix elements of the crystal field, the Zeeman energy for a field in the x -direction $-h_x J^x$, and also a term containing the quadrupolar moment $\lambda \mathcal{O}_2^2$, within the basis (1)–(4)

$$\mathcal{M}(\lambda, h_x, \Delta) = \begin{pmatrix} 0 & -2\sqrt{5/3}h_x & 0 & 0 \\ -2\sqrt{5/3}h_x & \Delta + 7\lambda & 0 & 0 \\ 0 & 0 & \Delta & -h_x/2 \\ 0 & 0 & -h_x/2 & \Delta - 7\lambda \end{pmatrix} \quad (7)$$

The field couples the singlet ground state $|\Gamma_1\rangle$ to the \mathcal{O}_2^2 -moment bearing excited state $|\Gamma_4^+\rangle$. Therefore in the presence of a magnetic field, uniform quadrupolar moment is no longer "spontaneous". If at $H = 0$, we had to do with a transition to a ferroquadrupolar state, it would be smeared

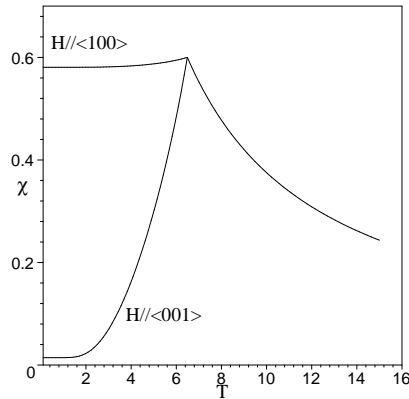


Figure 1. The temperature dependence of the magnetic susceptibility. The onset of \mathcal{O}_2^2 -type quadrupolar order makes the two $H \parallel z$ and $H \parallel x$ behavior inequivalent.

out in $H \neq 0$, and we no longer had a phase boundary to speak about⁵. However, for *antiferroquadrupolar* coupling, the appearance of the staggered quadrupolar moment is still symmetry breaking, and therefore a sharp phase transition remains possible also in an external magnetic field. Therefore, if we had no other evidence than that $\text{PrFe}_4\text{P}_{12}$ has sharp phase transitions in external magnetic field, and we adopted the Γ_1 – Γ_4 scheme, we would have to conclude that the ordered state could not be ferroquadrupolar, but only antiferroquadrupolar.

2.3. MEAN FIELD RESULTS

Doing the mean field theory [3] for AFQ ordering involves diagonalizing matrices like (7), and we do not give the details here.

Fig. 1 illustrates that an AFQ transition, though of non-magnetic nature, may give a susceptibility which looks very much like what you expect from an antiferromagnet. The cubic (001) and (100) directions are equivalent in the para phase but the appearance of \mathcal{O}_2^2 -type AFQ order makes the x -field susceptibility appear as "transverse", while the z -field susceptibility looks "longitudinal". Of course, instead of $\mathcal{O}_2^2 = J_x^2 - J_y^2$ we might have chosen $J_y^2 - J_z^2$ or $J_z^2 - J_x^2$, so in a crystal one would expect an equal mixture of the corresponding AFQ domains, and the susceptibility suitably averaged. The experiments may be taken to correspond to this.

⁵ Purely in symmetry terms: applying a field in one of the cubic (100) directions, the symmetry would be lowered to C_{4h} , and the decomposition of Γ_4 of O_h in terms of the irreps of C_{4h} would contain the identity which also comes from Γ_1 ground state.

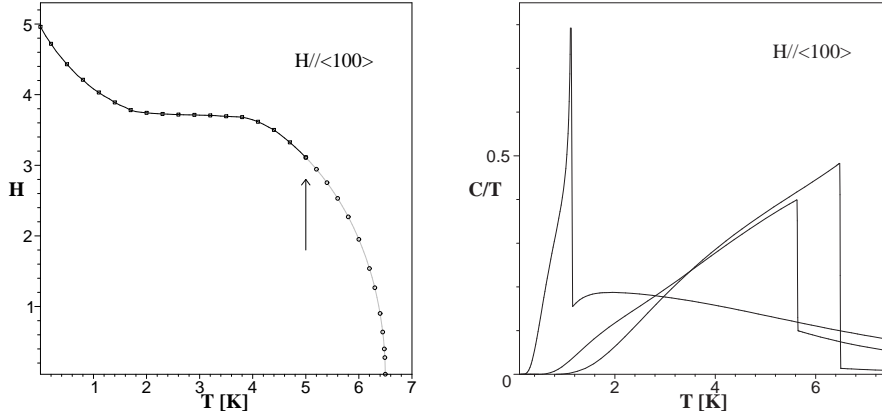


Figure 2. *Left:* The boundary of the antiferroquadrupolar phase in the H - T plane. The curve is drawn in black for first-order transitions, and in grey for continuous phase transitions. Arrow indicates the tricritical point. *Right:* The T -dependence of the temperature coefficient of the specific heat for $H = 0, 2.5$, and 4 Tesla (in order of decreasing transition temperatures).

Fig. 2 (left) gives the phase diagram. The crystal field splitting Δ and the quadrupolar coupling λ were chosen so as to get at least a rough numerical agreement with the experimental phase diagram [11]. There is still some freedom in the parameters, but we found that a rather low $\Delta \approx 4-6$ K has to be chosen (with $z = 8$, $\lambda \approx 0.08 k_B$), if we want to get both $T_{tr}(H = 0)$ and the tricritical point right. These estimates are likely to be subject of some revision when further (especially dipolar) couplings are allowed for. – In spite of an overall similarity to the phase diagram based on experiments, we note that the low- T , high- H upcurving part of our present phase boundary represents a deviation, the reason for which remains to be clarified.

The changeover to a regime of first-order transitions in higher fields is evident in the field dependence of the specific heat; the curves shown in Fig. 2 (right) bear a close resemblance to the measured ones. The same is true of the magnetization curves (Fig. 3) where we see a change from the regime of sharp metamagnetic transitions at low temperatures to continuous phase transitions at intermediate T 's, and eventually smooth behavior in the para phase.

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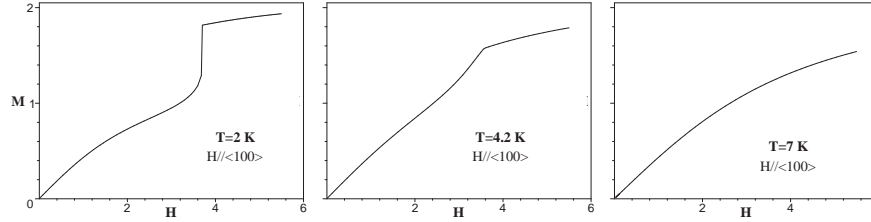


Figure 3. Antiferroquadrupolar order underlies the sharp metamagnetic transition at low T (left). With increasing T , we pass through second order transitions (middle) to smooth behavior (right).

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References

1. C.D. Batista et al., Phys. Rev. **B65**, 180042(R), 2002, and references therein.
2. A.T. Boothroyd, J. Alloys and Compounds 303-304, 489, 2000.
3. A. Kiss and P. Fazekas, to be published.
4. R. Shiina et al., J. Phys. Soc. Japan **66**, 1741, 1997.
5. A. Takahashi, H. Shiba, J. Phys. Soc. Japan **69**, 3328, 2000.
6. G. Mihály et al., Phys. Rev. **B61**, R7381, 2000; G. Mihály et al., at this conference.
7. K. Penc et al., to be published.
8. P. Fazekas, Found. Phys. **30**, 1999, 2000.
9. P.W. Anderson, Mat. Res. Bull. **8**, 173, 1973; P. Fazekas and P.W. Anderson, Phil. Mag. **30**, 423, 1974.
10. K. Penc et al., at this conference.
11. Y. Aoki et al., Phys. Rev. B **65** 064446, 2002; J. Phys. Chem. Sol. **63**, 1201, 2002.
12. S.H. Curnoe et al, J. Phys. Chem. Sol. **63**, 1207, 2002; Physica B **312-313**, 837, 2002.
13. C. Sekine et al., Phys. Rev. Lett. **79**, 3218, 1997.
14. E.D. Bauer et al., Phys. Rev. B **65**, 100506(R), 2002; K. Miyake et al., unpublished; D.E. MacLaughlin et al., Phys. Rev. Lett. **89**, 157001, 2002.
15. K. Iwasa et al., Physica B **312-313**, 834, 2002.
16. Y. Aoki et al., J. Phys. Soc. Japan **71**, 2098, 2002.